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# Interpreting Organic Solute Transport Data from a Field Experiment Using Physical Nonequilibrium Models

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# INTERPRETING ORGANIC SOLUTE TRANSPORT DATA FROM A FIELD EXPERIMENT USING PHYSICAL NONEQUILIBRIUM MODELS

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## ABSTRACT

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## INTRODUCTION

Transport of hydrophobic organic chemicals by groundwater has been traditionally described using the advective/dispersive transport equation with a term to account for sorption of the organic solute onto the soil matrix. This sorption term is often developed assuming local equilibrium and a linear, reversible relationship between the quantity of chemical in the adsorbed and dissolved phases. Several investigators have found, in laboratory column studies, that the nearly symmetric, sigmoid forms of breakthrough curves predicted using models making these simplifying assumptions regarding sorption, do not agree with experimental observations (Van Genuchten and Wierenga, 1976; Rao et al., 1979; De Smedt and Wierenga, 1979). Experimentally observed breakthrough responses often exhibit highly asymmetric or nonsigmoid profiles, which will be referred to as tailing.

Either physical or chemical phenomena may cause tailing. That is, for physical and/or chemical reasons, one or more of the linear, reversible, equilibrium sorption assumptions may not hold, resulting in the inapplicability of the advection/dispersion model.

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When tailing is thought to occur due to a physical phenomenon, it has been hypothesized that because of soil aggregation, slow flow, or unsaturated flow, zones of immobile water exist (Van Genuchten and Wierenga, 1976). Slow diffusion of solute through these zones leads to a (physically) kinetically limited sorption process.

In the field experiment discussed in this paper, the porous medium is apparently unaggregated and saturated, yet extensive tailing of breakthrough responses is observed for the more strongly sorbed solutes. The chemical assumption of linear equilibrium sorption was experimentally verified in the laboratory. Comparison of sorption and desorption equilibria indicates that the process is essentially reversible (Curtis, 1984).

Simulations done with physical nonequilibrium models indicate that the observed tailing may be explainable using such models. Relatively small zones of immobile water may result in extensive tailing, if sufficient sorption capacity exists in these zones.

In this paper, two such physical nonequilibrium models are examined. The two nonequilibrium models used are: (1) A first-order kinetic model, which uses a first-order rate law to describe the rate of solute transfer between "mobile" and "immobile" zones of water; and (2) a spherical diffusion model which describes solute transfer by Fick's second law of diffusion within spherical immobile zones.

Simulations calculated using these two models will be compared with experimental observations, as well as with predictions of the traditional advection/dispersion model presuming local equilibrium. Also, the advantages and disadvantages of each of the two physical nonequilibrium models will be discussed.

## FIELD EXPERIMENT

In August 1982, a known mass of selected solutes was injected as a pulse into an uncontaminated portion of an unconfined, glaciofluvial sand aquifer at Canadian Forces Base Borden in Ontario, Canada (Mackay et al., 1985). The injected solution contained two conservative tracers (chloride and bromide) and five halogenated organic compounds (carbon tetrachloride, tetrachlorethylene, bromoform, o-dichlorobenzene, and hexachloroethane).

Using a pattern of nine injection wells in two rows, it was intended that the injection pulse have the form of a rectangular solid. Figure 1 shows the idealized pulse, and the locations of the three wells used for time-series concentration (breakthrough) sampling. The three breakthrough wells were sampled 2—3 times weekly, with a total of almost 200 samples taken from each well over the course of nearly 1—1/2 yrs. The samples were analyzed for the chloride and bromide tracers, as well as for the organic solutes.

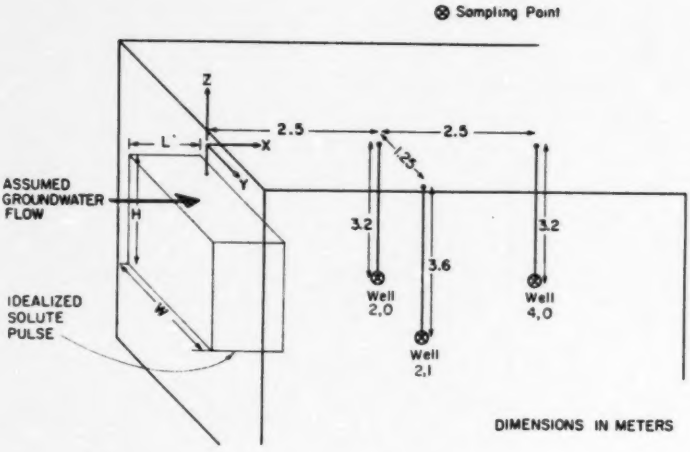


Fig. 1. Configuration of the injected pulse and the time-series sampling points.

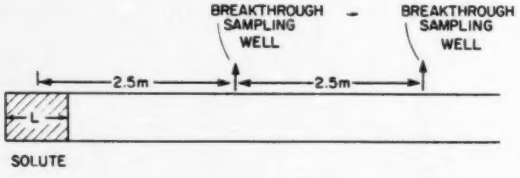


Fig. 2. Simplified one-dimensional representation for the breakthrough analysis.

If we assume one-dimensional flow, and neglect transverse dispersion in the $y$ and $z$ directions, the three-dimensional picture of Fig. 1 can be represented by the simplified one-dimensional form shown in Fig. 2.

## THEORY

In one dimension, solute transport through a porous medium is normally described using the advective/dispersive transport equation with a sorption term (Lapidus and Amundson, 1952):

$$\theta \frac{\partial C}{\partial t} = \theta D \frac{\partial^2 C}{\partial x^2} - \theta v \frac{\partial C}{\partial x} - \rho \frac{\partial S}{\partial t} \tag{1}$$

where $C(x,t)$ represents the aqueous solute concentration (kg solute in solution per $m^3$ water); $S(x,t)$ is the sorbed solute concentration (kg solute sorbed per kg soil); $\theta$ is the aquifer porosity ($m^3$ water per $m^3$ bulk volume);

$D$ is the dispersion coefficient ($m^2$ per day); $v$ is the average flow velocity (m per day); $\rho$ is the bulk soil density (kg soil per $m^3$ bulk volume); $x$ is the spatial coordinate (m); and $t$ is time (day). If linear, reversible, equilibrium sorption is assumed, sorbed and aqueous solute concentrations may be related using the concept of a partition or distribution coefficient, $K_d$, such that:

$$S = K_d C \tag{2}$$

where $K_d$ = (kg solute sorbed per kg soil)/(kg solute in solution per $m^3$ water). With these assumptions, a dimensionless retardation factor, $R$, can be defined:

$$R = 1 + \frac{\rho}{\theta} K_d \tag{3}$$

so that eqn. (1) can be rewritten:

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \tag{4}$$

Analytical solutions to eqn. (4) may be found in the literature for a variety of initial and boundary conditions (Van Genuchten and Alves, 1982). Assuming that a uniform slug of solute, having width $L$ (m) and concentration $C_0$ (kg solute per $m^3$), was injected into the Borden aquifer, and that no background levels of solute existed in the aquifer prior to injection, the following initial and boundary condition equations may be written:

$$\left.\begin{aligned} C(x,0) &= C_0 \quad -\frac{L}{2} \leqslant x \leqslant \frac{L}{2} \\ &= 0 \quad\quad x > \frac{L}{2} \\ -D \frac{\partial C\left(-\frac{L}{2}, t\right)}{\partial x} &+ vC\left(-\frac{L}{2}, t\right) = 0 \\ \frac{\partial C}{\partial x}(\infty, t) &= 0 \end{aligned}\right| \tag{5}$$

Lindstrom and Boersma (1971) presented an analytical solution to eqn. (4) for the initial and boundary conditions shown in eqn. (5). Note that this solution is for the simple case of one-dimensional transport.

From the above discussion, it is clear that assuming linear, reversible, equilibrium sorption vastly simplifies the solution of eqn. (1). In the Palo Alto Baylands study of organic solute transport (Roberts et al., 1984) the simplified transport model, presuming local equilibrium for sorbing solutes,

sufficed for simulating solute concentration histories. However, it has been noted in other investigations (Kay and Elrick, 1967; Green et al., 1972; Van Genuchten and Wierenga, 1977; Nkedi-Kizza et al., 1982) that experimentally obtained breakthrough responses exhibited sharper initial breakthrough and more tailing than would be predicted using models that assume linear, reversible, equilibrium sorption. Because of this apparent inadequacy of the simple advection/dispersion model, more complex models were evaluated.

Figure 3 schematically shows the basis for physical nonequilibrium models. Figure 3 shows zones of mobile water through which solute is transported by the mechanisms of advection and dispersion. Considering a sorbing solute, and assuming sorption sites are distributed on the mineral grains, it can be seen from Fig. 3 that a certain fraction ($f$) of sorption sites is in direct contact with mobile water. Solute sorption onto these sites is assumed to be linear, reversible, and at equilibrium.

The remaining water depicted in Fig. 3 is classified as immobile. This water may exist in dead-end pores, in layers of low permeability, trapped in aggregates, or as thin external layers surrounding the mineral grains. It is assumed that the velocity of water in these immobile zones is orders of magnitude less than the mobile water velocity, $v_m$ (m per day). Thus, solute is presumed to be transported through these zones solely by the mechanism of diffusion. These zones act as diffusion sources/sinks for solute flowing in the mobile regions. Assuming linear, reversible, equilibrium sorption for solute within the immobile zones, as well as for the "mobile" solute, and performing a mass balance for solute in the mobile region, one finds:

$$R_m \theta_m \frac{\partial C_m}{\partial t} = \theta_m D_m \frac{\partial^2 C_m}{\partial x^2} - \theta_m v_m \frac{\partial C_m}{\partial x} - \theta_{im} R_{im} \frac{\partial \overline{C}_{im}}{\partial t} \qquad (6.1)$$

where $\theta_m$ and $\theta_{im}$ are the pore volumes of mobile and immobile water, respectively, with $\theta_m + \theta_{im} = \theta$; $C_m(x,t)$ and $\overline{C}_{im}(x,t)$ are the average aqueous concentrations of solute in the mobile and immobile waters ($kg\,m^{-3}$); $D_m$ is the dispersion coefficient for the mobile zone ($m^2$ per day); $v_m$ is the average flow velocity in the mobile zone (m per day); $R_m$ and $R_{im}$ are the retardation factors in the mobile and immobile zones, respectively, defined as:

$$R_m = 1 + \frac{f \rho K_d}{\theta_m} \qquad (6.2)$$

and:

$$R_{im} = 1 + \frac{\rho(1-f)K_d}{\theta_{im}} \qquad (6.3)$$

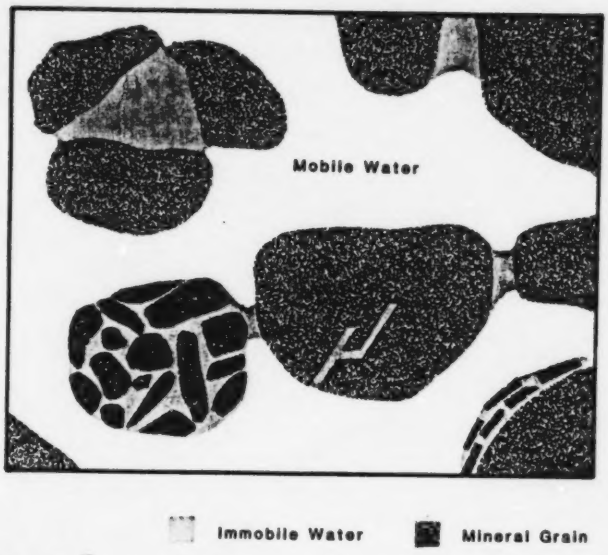


Fig. 3. Conceptual schematic of mobile and immobile zones assumed in physical non-equilibrium models.

The third term on the right-hand side of eqn. (6.1) represents accumulation of solute within immobile zones. The assumptions made in defining this term lead to different physical nonequilibrium models.

The simplest physical nonequilibrium model makes the assumption that the immobile water zones are perfectly mixed, such that $\overline{C_{im}} = C_{im}$ where $C_{im}$ is the solute concentration at any point within the immobile zone, and that transfer of solute between mobile and immobile regions is governed by a first-order rate equation. These assumptions are mathematically shown below:

$$\theta_{im} R_{im} \frac{\partial \overline{C_{im}}}{\partial t} = \alpha(C_m - \overline{C_{im}}) \tag{7}$$

where $\alpha$ is the first-order rate constant (per day). Combining eqns. (6) and (7) with appropriate initial and boundary conditions mathematically describes what will be referred to as a first-order kinetic, physical non-equilibrium model. Such first-order models have been described by Coats and Smith (1964) and Van Genuchten and Wierenga (1976).

Another set of assumptions that can be made regarding the immobile zone accumulation term in eqn. (6) is that: (a) the zones of immobile water are spheres of radius $a$; (b) the concentration of solute within the immobile zone at the outer radius of the sphere, $C_{im}(x,a,t)$, equals the mobile zone concentration, $C_m(x,t)$, at that point; and (c) solute transfer

in the immobile zone is governed by Fick's law of diffusion within a sphere. Mathematically, these three assumptions can be written:

$$\left.\begin{aligned} \overline{C_{\mathrm{im}}}\,(x,t) &= \frac{3}{a^3}\int_0^a r^2 C_{\mathrm{im}}\,(x,r,t)\mathrm{d}r \\ C_{\mathrm{im}}\,(x,a,t) &= C_{\mathrm{m}}\,(x,t) \\ R_{\mathrm{im}}\,\frac{\partial C_{\mathrm{im}}}{\partial t} &= \frac{D_{\mathrm{e}}}{r^2}\,\frac{\partial}{\partial r}\left(r^2\,\frac{\partial C_{\mathrm{im}}}{\partial r}\right) \end{aligned}\right| \qquad (8)$$

where $D_e$ is the effective diffusion coefficient for the solute within the immobile water zone ($m^2$ per day), and $r$ is the radial coordinate (m).

Combining eqns. (6) and (8) mathematically describes what will be referred to as a spherical diffusion model. Spherical diffusion models have been adapted by Rao et al. (1980) and Nkedi-Kizza et al. (1982).

## RESULTS AND DISCUSSION

Figure 4 shows breakthrough responses for chloride and two organic solutes obtained from well 4,0, approximately 5 m downgradient from the injection zone, sampling at a depth of about 3.2 m. Freyberg (1985) demonstrated that the chloride and bromide tracers behaved similarly in all important respects, and thus the bromide data are omitted from this

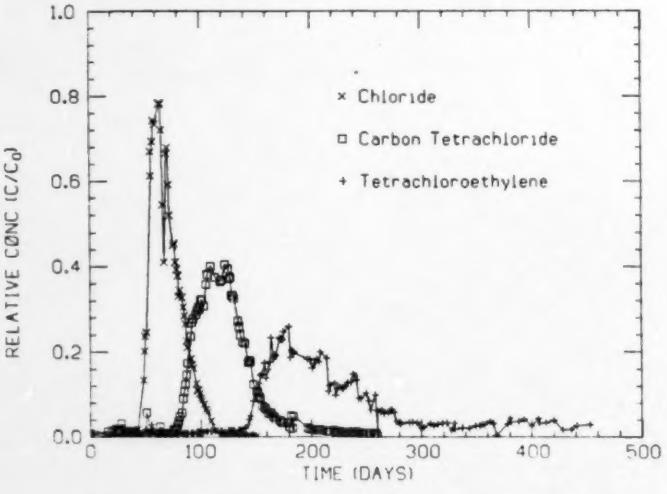


**Fig. 4. Breakthrough responses for chloride, carbon tetrachloride, and tetrachloroethylene at well 4.0 ($x = 5.0$ m, $y = 0.0$ m, $z = -3.26$ m).**

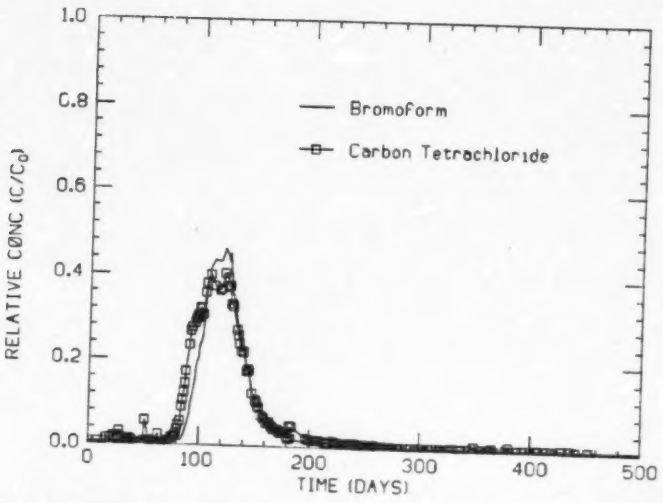


Fig. 5. Comparison of carbon tetrachloride and bromoform breakthrough responses at well 4,0 ($x = 5.0$ m, $y = 0.0$ m, $z = -3.26$ m).

paper for simplicity. Figure 4 plots normalized concentrations versus time, where normalized concentration is the measured concentration of solute divided by the concentration of solute initially injected into the aquifer ($C_0$). $C_0 = 892\,\text{mg}\,\text{l}^{-1}$, $30.7\,\mu\text{g}\,\text{l}^{-1}$, and $30.2\,\mu\text{g}\,\text{l}^{-1}$ for chloride, carbon tetrachloride, and tetrachloroethylene, respectively. The breakthrough responses shown in Fig. 4 are typical of the responses which were observed at the other two breakthrough sampling wells located within 5 m of the injection zone. Other breakthrough sampling wells are located further downgradient, but data from these more distant wells are presently incomplete.

The breakthrough reponses in Fig. 4 exhibit the chromatographic separation predicted by eqn. (1), the general advection/dispersion model with a sorption term. In this general model, sorbing solute transport is retarded, due to the fact that at any instant a portion of the solute is sorbed, and therefore immobile. The stronger the sorption, the greater the retardation, producing a chromatographic separation effect. In Fig. 4, we observe that chloride, presumed to be a conservative tracer travelling at the velocity of the groundwater, breaks through first. Carbon tetrachloride, a sorbing solute, is transported at a lower velocity and breaks through next. Later, tetrachloroethylene, which was found in laboratory experiments to be more strongly sorbed onto the aquifer material (Curtis, 1984), breaks through. Bromoform (omitted from the figure for clarity), which was also injected into the aquifer, had a breakthrough response almost identical to the carbon tetrachloride curve (Fig. 5). The other two injected solutes, hexachloroethane and o-dichlorobenzene, were not observed at the

breakthrough sampling wells in significant concentrations, presumably because of chemical or biological transformation (Roberts et al., 1985), so breakthrough responses for these two solutes are unavailable.

An interesting property of the breakthrough responses shown in Fig. 4 is the increase in skewness (tailing) with increasing sorption strength. The non-sorbed chloride tracer exhibits only minor asymmetry, whereas tetrachloroethylene is significantly skewed, with extended tailing. As has been noted previously, skewed breakthrough responses are predicted by physical nonequilibrium models. In particular, Van Genuchten and Wierenga (1976) showed that a physical nonequilibrium model would predict the observed increased tailing with increased distribution coefficient.

Figure 6 compares simulations of the breakthrough response data from well 4,0 using the advection/dispersion and first-order kinetic models. For the advection/dispersion model, a best fit was visually obtained using an analytical solution to eqns. (4) and (5) (Lindstrom and Boersma, 1971). $D$, $R$, and $v$ were used as fitting parameters. Values for these parameters are listed in Table 1. $D$ and $v$ were chosen so as to provide a best fit for all three solute breakthrough curves. The value of $R$ was separately varied to provide a best fit for each of the two sorbing solutes. For the chloride tracer (Fig. 6A), $R$ was set equal to unity.

In a similar fashion, an analytical solution to the first-order kinetic model described by eqns. (6) and (7) (Lindstrom and Narasimhan, 1973) was visually matched to the data. $D_m$, $v_m$, $\alpha$, $\theta_m/\theta$ (defined as $\phi$), and $f$ were chosen to fit all three solute breakthrough curves, whereas $R$ was separately varied to obtain a best fit for each of the two sorbing solutes.

Examining Fig. 6, it is apparent that, especially for the two sorbing solutes (Figs. 6B and C), the advection/dispersion model fails to describe the sharp breakthrough and tailing, whereas the first-order kinetic model simulation exhibits these salient characteristics of the data. Consideration of the parameter values (Table 1) raises several interesting points:

(1) The values of $D$ relative to $D_m$ and $v$ relative to $v_m$ depend on the model structure. If we assume that zones of immobile water are a real phenomenon, then the simple advection/dispersion model must incorporate the effect of these zones into the parameters $D$ and $v$. Hence, the parameter $D$ in the advection/dispersion model lumps the dispersion within the mobile water ($D_m$) together with any additional dispersion caused by the existence of immobile water. Baker (1977) showed that for long columns, the parameters in a first-order kinetic model are related to the value of $D$ in an equivalent advection/dispersion model by the following expression:

$$D = \phi D_m + \frac{(1-\phi)^2 (\theta_m v_m)^2}{\alpha\theta} \tag{9}$$

Substituting the fitted first-order kinetic model parameter values into the right-hand side of eqn. (9), we find $D = 0.006\,m^2$ per day, which overestimates the value of $D$ (Table 1) arrived at by fitting an advection/

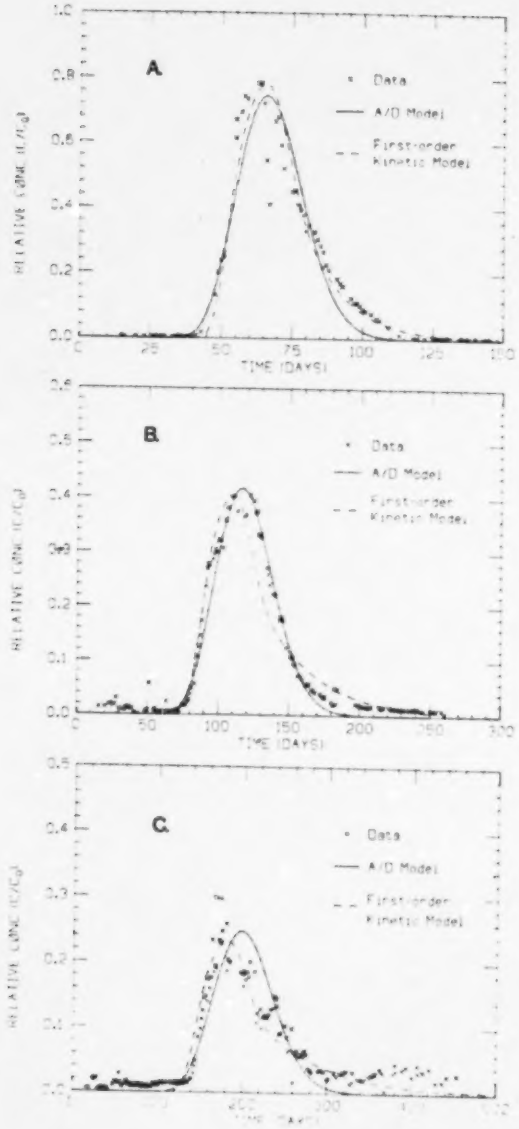


**Fig. 6. Comparison of first-order kinetic model and advection/dispersion model with experimental observations. (A) Chloride; (B) carbon tetrachloride; (C) tetrachloroethylene.**

TABLE 1

Parameter values used in simulations

| Parameter | Parameter values | | |
|---|---|---|---|
| | Advection–dispersion model | First-order kinetic model | Spherical diffusion model |
| Flow velocity | | | |
| $v$ (m per day) | 0.075 | [a] | [a] |
| $v_m$ (m per day) | [a] | 0.080 | 0.080 |
| Dispersion coefficient | | | |
| $D$ ($m^2$ per day) | 0.004 | [a] | [a] |
| $D_m$ ($m^2$ per day) | [a] | 0.001 | 0.001 |
| Retardation factors, $R$ | | | |
| chloride | 1.00 | 1.00 | 1.00 |
| carbon tetrachloride | 1.80 | 1.80 | 1.80 |
| tetrachloroethylene | 3.00 | 3.00 | 3.00 |
| Mobile zone fractions | | | |
| pore water, $\phi$ | 1.00[b] | 0.90 | 0.90 |
| sorption sites, $f$ | 1.00[b] | 0.80 | 0.80 |
| Exchange rate parameters | | | |
| kinetic rate constant, $\alpha$ (per day) | [a] | 0.004 | [a] |
| diffusion rate constant, $D_e/a^2$ (per day) | [a] | [a] | 0.007 |

[a]Not applicable; [b] not needed for simulations, but implicit in model.

dispersion model to the data by about 50%. However as noted by Baker (1977), the value of $D$ calculated using eqn. (9) will be overestimated for values of the dimensionless group $Pe = v_m x_0/D_m$ less than 1000, where $x_0$ is the travel distance of the solute plume to the sampling point. Since in our case, at $x_0 = 5$ m, $Pe = 400$, the overestimation of $D$ is not surprising.

Similarly, the parameter $v$ in the advection/dispersion model lumps the velocity of the mobile water ($v_m$) with the effect on velocity of the immobile regions. Since the immobile water is stagnant, we would expect the parameter $v$ to be less than $v_m$. The fitted values of $v$ and $v_m$ have this relationship (Table 1).

More quantitatively, we can define a diffusion time constant ($1/\alpha$) and an advection time constant ($x_0/v_m$) for a conservative tracer. For relatively small advection times, solute will not have had time to be affected by the diffusion mechanism, so the observed velocity of the solute will be the velocity of the mobile water ($v = v_m$). At relatively large advection times, when the solute has had an opportunity to fully diffuse into the immobile regions, we would expect the observed solute velocity to be the weighted

TABLE 2

Comparison of retardation factors

| | Laboratory estimate[a] | Curve fitting |
|---|---|---|
| bromoform | 1.7 | 1.8 |
| carbon tetrachloride | 1.7 | 1.8 |
| tetrachloroethylene | 3.1 | 3.0 |

[a]Estimated from sorption equilibrium experiments (Curtis, 1984).

average of the mobile and immobile water velocities. Since the immobile water velocity is by definition zero, we would expect $v = v_m \phi$. Thus, for our particular parameters, where the advection time constant of 62 days is comparable to the diffusion time constant of 250 days, we expect the advection/dispersion model parameter $v$ to have a value between $v = v_m = 0.08$ m per day and $v = v_m \phi = 0.072$ m per day. Our fitted parameter values exhibit this relationship.

(2) The values of $R$ obtained from curve fitting are similar to the $R$ values derived from batch equilibrium sorption experiments conducted by Curtis (1984) using Borden aquifer material (Table 2).

(3) For an aggregated soil, Nkedi-Kizza et al. (1982) measured values of $\phi$ of about 0.6. Baker (1977) notes values of $\phi = 0.9$ in oil reservoirs. The $\phi$ value of 0.9 obtained here agrees reasonably well with previous work.

(4) Comparison of $f$ and $\phi$ values suggests that sorption sites are slightly more concentrated in the immobile zone. If sorption sites are uniformly distributed throughout the mobile and immobile regions, $f$ would equal $\phi$. If all sorption sites were within the immobile region, as was postulated by Nkedi-Kizza et al. (1982) for an aggregated Oxisol soil, then $f = 0$. In the unaggregated sandy soil at Borden, it is reasonable to postulate that the fraction of sorption sites adjacent to mobile water, $f$, is given more nearly by $f = \phi$ than by $f = 0$. The values of $\phi$ and $f$ obtained from curve fitting (Table 1) seem reasonable in light of this.

(5) The value of the first-order rate constant $\alpha$ is the same for all three solutes. Since the rate constant presumably depends on the diffusion coefficient of the solutes, and the two organic solutes have diffussion coefficients within 10% of each other (using the Wilke-Chang correlation to calculate the coefficients), it seems physically realistic that the rate constants for the two organics are approximately equal. It is less apparent, however, why chloride, which has a diffusion coefficient approximately 2.5 times greater than the diffusion coefficients of the organics, should have the same rate constant. One possible explanation is that diffusion of the chloride anion in the soil is hindered by charge effects, whereas diffusion of the neutral organic molecules is unaffected. Anion exclusion of chloride has been documented in the literature (Thomas and Swoboda, 1970; Krupp et al., 1972; Bresler,

1973). In the absence of measured values, it does not seem unreasonable to assume the rate constant of chloride to be equal to the organic rate constants.

In precisely the same way as described above for the first-order kinetic model, the parameter values for the spherical diffusion model were obtained. The same parameters were used for fitting, except that instead of using a first-order rate constant $\alpha$, the rate parameter $(D_e/a^2)$ was estimated by fitting simulations to the data. Parameter values are shown in Table 1. A Crank-Nicolson finite difference solution to eqns. (6) and (8) was used in the fitting process. Time and space increments ($\Delta t$ and $\Delta x$, respectively) were chosen using the following criterion suggested by Barovic and Boochs (1981) to eliminate overshooting and reduce inaccuracy:

$$\frac{v_m \Delta x}{D_m} \leqslant 2 \qquad \frac{v_m \Delta t}{\Delta x} \leqslant 2 \tag{10}$$

Comparison of the finite difference simulations using very high and very low values of the rate parameter with analytical solutions of the advection/dispersion equation showed the method to be accurate. Figure 7 compares the advection/dispersion and spherical diffusion model simulations with the data from well 4,0 for the three solutes. As with the first-order kinetic model (Fig. 6), the spherical diffusion model (Fig. 7) better describes the tailing of the sorbing solute curves than does the advection/dispersion model.

Comparing the simulations of the physical nonequilibrium models (Figs. 6 and 7), there seem to be no striking differences between the two models. Both models simulate the sharp initial breakthrough, tailing, and increased skewness with increased sorption. The differences between the models have more to do with their formulation and use than with their results. The first-order kinetic model is quite simple to use, requiring much less computational effort than the spherical diffusion model (Van Genuchten, 1985). On the other hand, the spherical diffusion model is more firmly founded on a physical basis, and is more amenable to independent determination of parameters (Rao et al., 1980).

## SUMMARY AND CONCLUSIONS

Observations have been presented from a solute transport experiment conducted under conditions of natural groundwater flow. The solute behaviour shows evidence of deviation from that anticipated based on a commonly used, simplified form of the transport equation. The deviations expressed themselves as extended tailing of breakthrough responses obtained by time-series sampling at discrete monitoring points. Such extended tailing was seen with nonsorbing as well as sorbing solutes, but appeared to be accentuated with increasing strength of sorption.

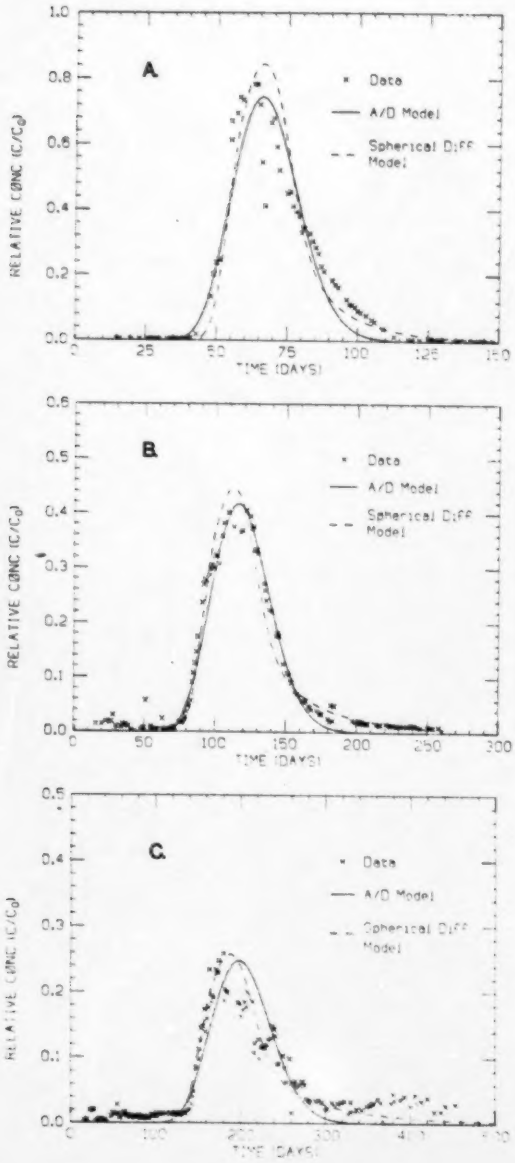


**Fig. 7. Comparison of spherical diffusion model and advection/dispersion model with experimental observations. (A) Chloride; (B) carbon tetrachloride; (C) tetrachloroethylene.**

Possible causes for the extended tailing are the following: (a) slow diffusion into fine fracture systems within the solid grains constituting the porous medium; (b) small aggregates of quasi-spherical shape, containing immobile water and sorption sites accessible only by diffusion; (c) immobile zones consisting of impermeable strata, rather than aggregates; (d) slow desorption kinetics, reflected for example as hysteretic sorption equilibria; and (e) nonlinearity of the sorption equilibria. In the case at hand, there is little supporting evidence for significant hysteresis or nonlinearity in sorption equilibrium. Therefore, arguments based on slow diffusion seem most promising as explanations of the observed tailing phenomena.

In this paper, two approaches are explored for simulating nonequilibrium behaviour: a spherical diffusion model and a first-order kinetic model. Curve fitting of the models to the data was done visually, and therefore parameter values are not necessarily unique. In the future, a more formal method of fitting will be applied. It is clear, however, that the nonequilibrium models capture the salient characteristics of the field experiment data much better than does the advection/dispersion model, with its assumption of local equilibrium. The two alternative nonequilibrium modeling approaches result in simulated responses that are similar in form. The diffusion model offers the advantage of incorporating information on the physical structure of the porous medium, with potential for independent parameter estimation. The first-order kinetic model relies exclusively on fitting to estimate the parameters, and hence is less amenable to being used in a predictive mode, but its mathematical simplicity affords economy in use, an important advantage especially in two- or three-dimensional applications.

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